

SULPHUR-CONTAINING PHENOL-FORMALDEHYDE RESINS TO MODEL THE THERMAL CHEMISTRY OF ORGANIC SULPHUR FORMS IN COALS

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ABSTRACT

Non-melting silica immobilised substrates have previously been used to investigate pyrolysis behaviour and were shown to be ideal calibrants for temperature programmed reduction (TPR), with the SiO-C linkage stable at temperatures above 500°C. An alternative class of materials that should prove equally suitable are phenol-formaldehyde resins which enable model moieties to be incorporated into a highly cross-linked matrix. A series of sulphur containing co-resites have been prepared using phenol with, as the second component, dibenzothiophene, diphenylsulphide, phenylbenzylsulphide and thioanisole. A mole ratio of 3:1 (phenol to sulphur-containing component) was adopted to ensure that a reasonably high degree of cross-linking was achieved in the initial preparation of the resoles. The formation of the resites by curing the resoles at 200°C was monitored by solid state ¹³C NMR. A resole has also been prepared from diphenyldisulphide but due to the comparable bond strengths of the S-S and C-O linkages, the curing temperature was reduced to 120°C to avoid cleavage of the disulphide bond. As well as being used as calibrants for TPR, the resites offer considerable potential for probing the influence of catalysts in hydropyrolysis and for investigating the effect of pyrolysis conditions on the interconversion of sulphides into thiophenes.

INTRODUCTION

In order to obtain insights into the complex reactions which occur during the pyrolysis and liquefaction of solid fuels, detailed structural information about the starting material and an understanding of how the different functionalities present behave under processing conditions are required. To achieve the latter aim, model compound studies performed in both the vapour and liquid phases have been used extensively ⁽¹⁾. However, a major drawback with such studies is the fact that the radicals generated via bond homolysis are mobile and free to diffuse independently prior to further reaction. In contrast, for solids such as coals and oil shales, many of the reactive intermediates remain covalently attached to the cross-linked macromolecular framework and thus their reactivity is subject to diffusional restraints.

In order to explore the effects of restricted mobility in multipathway free-radical reactions, Buchanan and coworkers pioneered work on model compounds immobilised on silica ^(2,4). Recently, a series of silica immobilised diphenylalkanes and sulphur-containing substrates have been used at Strathclyde to study solid fuel pyrolysis phenomena. In addition, the sulphur-containing substrates have been used as calibrants for temperature programmed reduction (TPR) ^(5,6); a technique based on the principle that different organic sulphur forms present in solid fuels have different characteristic reduction temperatures at which hydrogen sulphide (H₂S) evolves. Previously, the technique had met with only limited success, primarily because only

labile non-thiophenic forms were observed. Poor overall sulphur balances resulted, with virtually all the thiophenic sulphur remaining in the char due to the low pressures and the low boiling reducing agents used (7-10). Further, little account has been taken of the reduction of pyrite to pyrrhotite and retrogressive reactions, particularly the conversion of sulphides into thiophenes. These drawbacks have been overcome by the use of a well-swept fixed-bed reactor operating at relatively high hydrogen pressures (up to 150 bar) (11,12). Typically, over 70% of the organic sulphur is reduced to H_2S with the remainder being released in the tars. The use of effective catalysts, such as sulphided molybdenum can further improve the extent of desulphurisation (13).

In contrast to the reflux-type reactors used in low (atmospheric) pressure TPR studies (7-10) where liquids have been used for calibration, solids which do not soften prior to the onset of thermal decomposition are essential due to the nature of the well-swept high pressure reactor (5,6). In this respect, non-melting silica immobilised substrates are ideal, as demonstrated by immobilised benzene where the Si-O-C linkage was found to be stable to ca 500°C, even in reducing atmospheres (14). Immobilised samples of dibenzothiophene, diphenylsulphide, benzylphenylsulphide and thioanisole were subsequently prepared and used as calibrants (5,6) for both the well-swept high pressure and a reflux-type low pressure TPR reactor. Further, the substrates were found to be suitable for probing coal and oil shale pyrolysis mechanisms at temperatures in the range 400-600°C, generally used to maximise tar yields in both fluidised and well-swept bed reactors.

An alternative class of materials that should prove equally suitable are phenol-formaldehyde resins which offer the option of incorporating a wide variety of sulphur-containing moieties. A series of co-resites have been prepared using phenol together with a series of sulphur-containing precursors; 2-hydroxydibenzothiophene, *p*-hydroxydiphenylsulphide, 4-hydroxyphenylbenzylsulphide and 4-hydroxythioanisole, the same precursors used previously for the preparation of silica-immobilised substrates (5,6). A resole has also been prepared using dihydroxydiphenyldisulphide (DHPDS). This paper details the monitoring of the curing treatment by ^{13}C solid state NMR and the desulphurisation behaviour, of the formed resites, by high pressure temperature programmed reduction (TPR).

EXPERIMENTAL

Synthesis Thioanisole was the only commercially-available precursor used. 2-Hydroxydibenzothiophene was prepared via the base hydrolysis of the corresponding bromo derivative (15). Benzene sulphinic acid was reacted with phenol using a modification of Hinsberg's method (16) to prepare 4-hydroxydiphenylsulphide. 4-hydroxyphenylbenzylsulphide was prepared by reacting 4-hydroxythiophenol with benzylbromide (17). 4-hydroxythiophenol was oxidised with dimethyldithiobis(thioformate) to yield 4,4'-dihydroxydiphenyldisulphide (18).

The co-resites were prepared using the procedure described by Bar and Aizenshtat (19) with a phenol to formaldehyde mole ratio of 1:2.5. The mole ratio of phenol to the sulphur-containing component was 3:1 to ensure that a reasonably high degree of crosslinking was achieved in the initial resoles and ca 6 weight % sulphur was present in the final cured resites. Sodium hydroxide was used as catalyst in the condensation reaction with mole ratio of 0.1 with respect to phenol. The resites were cured in an oven purged with nitrogen gas at a temperature of 200°C. The resin containing DHPDS was prepared without addition of phenol and was partially cured at the much lower temperature of 130°C to avoid cleaving the disulphide bonds.

¹³C-NMR Analysis Solid state ¹³C NMR was used to follow the removal of the ether/alcohol functional groups which occurred during curing. Cross polarisation/magic-angle spinning (CP/MAS) spectra were obtained using a Bruker MSL100 instrument operating at 25MHz for carbon. A contact time of 1 ms and a recycle delay of 1.5s were employed.

High pressure TPR Details on the high pressure system are described elsewhere^(5,6,12,13). As previously, a hydrogen pressure of 150 bar was used with a heating rate of 5°C/min over the range 100-600°C. Typically, between 0.2 and 0.3 g of the resite (particle size range of ca 0.1-1.0 mm) was mixed with 2-3 g sand. Hydrogen sulphide and other volatiles evolved were detected on-line using a quadrupole mass spectrometer (VG Sensorlab, 0-300 a.m.u.).

RESULTS AND DISCUSSION

Characterisation of the co-resites The elemental compositions of the cured co-resites and the disulphide resole, together with their chloroform solubilities are listed in Table 1. These results indicate that the desired level of sulphur incorporation (ca 6% w/w) has been achieved and that the resites are macromolecular in character with chloroform solubilities below 1% w/w. The DHDPDS resole obviously contains a much higher sulphur content than the resites because of the disulphide linkage and the fact that phenol was not employed in the preparation.

Figure 1 shows the CP/MAS ¹³C NMR spectra for the partially-cured (130°C) phenylbenzylsulphide and dibenzothiophene co-resites and Figure 2 compares the spectra for the partially cured dibenzothiophene resole and the corresponding resite cured at 200°C. The spectra of all four fully cured co-resites are shown in Figure 3. Table 2 summarises the assignments for the peaks observed. In the initial resoles, the peaks at ca 60 ppm and 73 ppm attributable to methylol carbon directly attached to the ortho or para position of the phenol ring and dimethylene ether carbons, respectively, dominate over the methylene bridge carbon peaks. In addition, the resoles display another intense C-O peak at ca 93 ppm due to hemiacetal carbons (OCH₂O). For the resites cured at 200°C, the spectra only contain aliphatic carbon peaks centred at 35 and 18 ppm with no major discernible peaks at 70 ppm from ether linkages.

Figure 1 indicates that the spectra of the partially-cured resites still contain major aliphatic C-O peaks which necessitated the use of a significantly higher curing temperature to eliminate all of the ether linkages. The peak at 18 ppm observed in all the spectra of the co-resites in Figure 3 is attributable to arylmethyl and, for dibenzothiophene and diphenylsulphide, its intensity is approximately one-quarter of that for the methylene peak at 35 ppm. The intensity of the 18 ppm peak in the case of the thioanisole resite is somewhat greater due to the contribution from S-CH₃.

High pressure TPR Figures 4-8 show the high pressure TPR evolution profiles of H₂S (*m/z*=34), and, where appropriate, CH₃SH (*m/z*=48), benzene (*m/z*=78), toluene (*m/z*=91) and methane (*m/z*=16), obtained for the four co-resites investigated. Figure 5 also shows the H₂S evolution profile for the DHDPDS resole. In addition, the desulphurisation behaviour of the dibenzothiophene co-resite was also investigated with a sulphided molybdenum catalyst (nominal loading of 0.4% w/w Mo)^(13,14); the H₂S evolution profile is shown in Figure 4.

For dibenzothiophene (Figure 4), the H₂S profile is remarkably similar to that for the corresponding immobilised substrate with the temperature of maximum evolution (T_{MAX}) being close to 500°C⁽⁶⁾. The use of the sulphided Mo catalyst does not significantly affect the T_{MAX}

although the H_2S profile is surprisingly sharper. The continuation of the H_2S evolution profiles above $500^\circ C$ in both cases suggests that some condensation might be occurring to form larger thiophenic structures. The sulphur balance for the dibenzothiophene resite without catalyst, indicated that virtually 100% desulphurisation was achieved with *ca* 50% of the sulphur being released as H_2S with the remainder being in the tar collected.

The primary scission of the C-S bonds in the diphenylsulphide co-resite occurs at $330^\circ C$ (Figure 5), similar to the characteristic reduction temperature found for the immobilised substrate ⁽⁶⁾. The further release of H_2S at temperatures up to $600^\circ C$ indicates that much of the sulphidic sulphur has been converted into complex thiophenes. The initial reduction is accompanied by the evolution of CH_3SH and the onset of toluene evolution (Figure 5) possibly via reactions with the methylene bridges. It is interesting to note that no benzene evolves below $400^\circ C$ suggesting that the non-hydroxy substituted ring in the diphenylsulphide moieties may have been cross-linked by the curing process. The partially cured resole of DHDPDS gave a characteristic H_2S T_{MAX} below $300^\circ C$ (Figure 5) which is similar to that found previously for cysteine ⁽⁶⁾. However, the occurrence of secondary reactions leading to the formation of sulphides and complex thiophenes was indicated by over 70% of the H_2S evolving above $320^\circ C$.

For the phenylbenzylsulphide co-resite, initial H_2S evolution occurs at *ca* $280^\circ C$ (Figure 6) from the primary scission of the C-S bond. The extent of secondary chemistry is again considerably greater than found with the corresponding immobilised substrate ⁽⁶⁾. A significant amount of CH_3SH also evolves at $280^\circ C$ from the C-S scission, together with some methane and toluene (Figure 6). As with diphenylsulphide no benzene was observed at low temperature presumably because it is still bound via the methylene linkages to the remainder of the resite. Figure 7 indicates that, like its phenylbenzylsulphide counterpart, the thioanisole co-resite displays complex behaviour with the bulk of the H_2S evolving after the primary reduction of the C-S bond at *ca* $300^\circ C$. The initial H_2S release is accompanied by a considerable proportion of the sulphur evolving as methyl mercaptan.

General discussion Characteristic H_2S T_{MAX} s for the primary C-S bond scissions for the co-resites were very similar to their immobilised counterparts ⁽⁶⁾. However, the nature and extent of secondary reactions clearly differ in each case with the co-resites generally displaying a much greater extent of retrogressive chemistry. This may be due to the much larger particle size used (0.1-1 mm, cf. <0.05 mm) and possibly the generation of many more diverse radical species during pyrolysis. The co-resites are, by nature, much more convenient to use than the immobilised substrates and the focus of future research will be to investigate the effects of dispersed catalysts in vehicle-solvent liquefaction, hydrolysis and batchwise hydrogenation.

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Table 1 Elemental compositions and chloroform solubilities of the resites and the disulphide resole

Co-Resites/Resole	%C	%H	%S	% Solubility
Dibenzothiophene	72.3	4.2	5.4	< 1%
Diphenylsulphide	72.4	4.9	5.2	< 1%
Phenylbenzylsulphide	72.7	5.0	5.5	< 1%
Thioanisole	69.3	5.1	6.2	< 1%
Diphenyldisulphide	54.0	4.4	19.5	n.d

n.d = not determined

Table 2 ¹³C NMR peak assignments the resoles and resites

Chemical Shifts (ppm)	Functional Groups Assignment
18	Arylmethyl, ortho position relative to the OH group
30, 35 and 40	2,2', 2,4 and 4,4'-methylene carbon, respectively
58-65	Methylol carbon, ortho or para position relative to the phenol ring, ArCH ₂ OH
68-73	Dimethylene ether linkages; Ar-CH ₂ -O-CH ₂ -
95	Hemiacetals, OCH ₂ O
110-135	Phenolic ring carbons other than C-OH
152, 160	Phenolic, C-OH; C-O, aromatic ethers

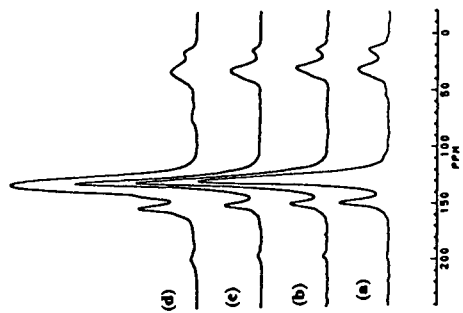
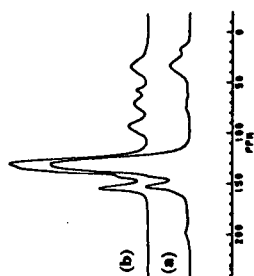
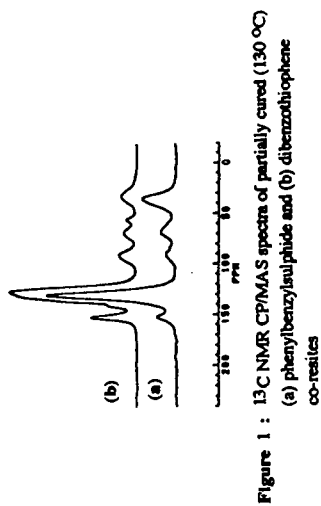


Figure 3 : ^{13}C NMR CPMAS spectra of fully cured (200 °C)
(a) thioanisole, (b) diphenylsulfide,
(c) phenylbenzylsulfide, (d) dibenzothiophene
co-resins

Figure 2 : ^{13}C NMR CPMAS spectra of (a) fully cured (200 °C)
and (b) partially cured (130 °C) dibenzothiophene co-resin

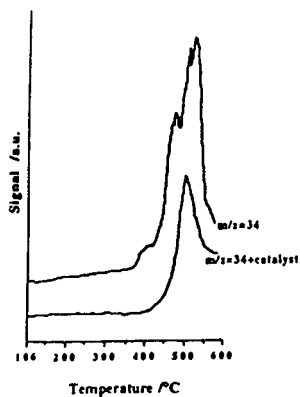


Figure 4: Hydrogen sulphide ($m/z=34$) evolution profiles for dibenzothiophene co-resite with and without catalyst

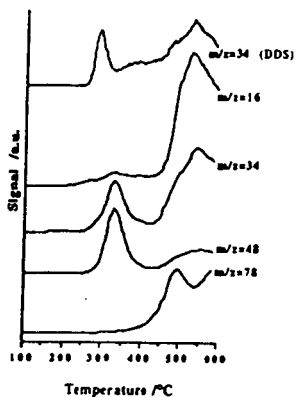


Figure 5: Evolution profiles for diphenylsulphide ($m/z=16, 34, 48$ and 78) and $m/z=34$ for diphenyldisulphide (DDS)

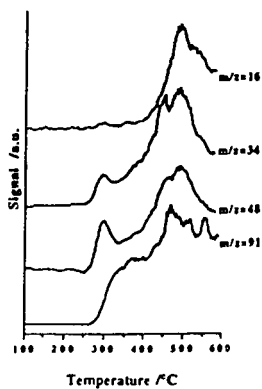


Figure 6: Evolution profiles for phenylbenzylsulphide ($m/z=16, 34, 48$ and 91)

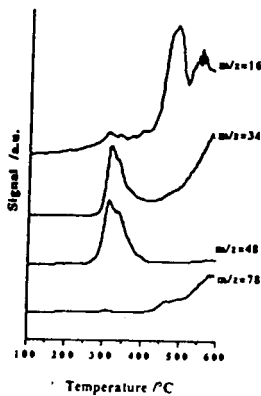


Figure 7: Evolution profiles for thioanisole ($m/z=16, 34, 48$ and 78)